Dear Dr. Warner:

When you submitted your paper (….migration of Marcellus-like brine…) you joined into one of the most important geological debates so far in the 21st Century. The debate can be framed any of a number of ways such as "Should America embrace its newfound abundance of natural gas?" Your paper cited *Nature's* version of the same question, "Natural Gas: Should fracking stop?" Shale gas production has such huge implications for America both economically and environmentally that papers joining the debate require an unusually close, detailed review.

My review is predicated on the objective of your paper which is stated as a search for "…specific areas of shale-gas development in northeastern Pennsylvania that are at increased risk for contamination of shallow drinking water resources with deeper formation brines…" (the last sentence of your abstract). The term, risk, suggests that your paper veers from a conventional geology paper and enters into the realm of science-based advocacy or if you like, science policy. You understand that by veering into science policy your work will be measured against a higher standard than that applied to a conventional review. The question is whether your objective has merit based on our understanding of brine circulation in the Appalachian Basin or whether this objective is more a leap of faith characteristic of advocacy-based science.

The debate over shale gas is polarizing and has had the effect of driving papers close to the line dividing science-based advocacy and advocacy-based science. Yours is no exception. For starters, you understand that red flags immediately emerge with your title (i.e., ….migration of Marcellus-like brine…) and the terms "Marcellus and Utica Brines" in the key to your Figure 2. To the best of my knowledge, yours is the first time anyone has attempted to register the term, "Marellus-like brine" into the geological literature. This expression will clearly inflame those folks who feel that gas extraction is dangerous and should be shut down. Your title puts you dead center on the science-based advocacy/ advocacy-based science line. Do you really want to be anywhere near that line?

The reviewer is left of decide from the evidence you present **whether the geology of the Appalachian Basin is such that gas industry activities can drive natural deep brine upwards to cause a salinization of shallow groundwater on a time scale that matters**. Let me pose a series of about a dozen questions in an attempt to allow you judge for yourself whether you have demonstrated such a risk (science-based advocacy) or whether your paper was unwittingly written to inflame the anti-drilling crowd (advocacy-based science).

First, there is the question of the significance of brines in the Appalachian Basin. Everyone agrees that the occurrence of saline water in rocks of the Appalachian Basin at depths over 500 feet BLS has been

known for over 50 years (Feth, 1962). So, finding saline water below fresh water throughout NE PA is no surprise. It is also no surprise that some of this saline water with Br and other components typical of Appalachian Basin brines would move into the upper part of the rock section through intermediate and regional scale flow systems to occasionally discharge as seeps and springs particularly in valleys. This is what Toth (1962) first theoretically showed and which has been shown observationally to be true many times since. There is general agreement that in the Appalachian Basin the interaction of regional circulation and brine originating as part of the formation of the Silurian Salina salts was responsible for much of the salinity in the production water that you cite as deep brines of the Appalachian Basin. "The brines are believed to have originated as the residual pore fluid in halite evaporates, probably the salts of the Silurian Salina Group" (Dresel and Rose, 2010). These brines were mobilized out of the salt during compaction by overlying beds and further tectonic compaction during Alleghanian decollement tectonics (Scanlin and Engelder, 2003). The volume of brine in the Appalachian basin is not surprising because the area sits on in excess of 100 Km^3 of salt in the Silurian Salina Formation which is found less than 300 m below the Marcellus. In this regard, residual brines originating as remaining fluids from the Salina salt deposition (not from the Marcellus) dictates the chemistry of regional groundwater patterns. In this regard, your title would be both more honest and more accurate with "……migration of Salina derived-brine….." It is important to emphasize the occurrence of highly saline brine with the characteristics of your "Marcellus type" throughout the Paleozoic section in northern and western PA (and NY, WV, OH and elsewhere). This is the region with Salina salt in the stratigraphic section.

<u>Second, there is the question scale time and what length of time matters in judging the risk that industrial activity will cause deep brine to contaminate ground water</u>. As a given, everyone agrees that deep basin circulation can occur over time scales of millions of years and that there is a connectivity between shallow and deep-subsurface waters in NE-PA on this longer time scale. On page 9 you imply that deep basin fluid migration occurs "on an undetermined timescale". This is not true because hydrologists have dated, modeled and understood the timescale for deep basin migration based on volumes of literature (see Bethke's papers as an example). One example might be emplacement of the oil tar in the Athabasca sands by migration of hundreds of km from of the deep Canadian foreland following the Sevier Orogeny in the late Cretaceous (this goes back to Toth's work). Another example within NE PA is the dissolution of the salt pillow under the Lackawanna Syncline by deep basin migration from hinterland to foreland (Harrison et al., 2004: GSAB). The foreland to which I refer is your sample area through which more than 7 Km^3 of salt was moved by dissolution in a regional flow network out of the core of the Appalachian Mountain Belt? Furthermore, Dresel and Rose (2010) find that essentially all the deep brine has mixed with more dilute waters, indicating that it has migrated up from the Salina thru Marcellus into shallower formations but on a time scale of over 200 million years. Of course, you understand that mixing is indicated by the fact the no brine has the composition of their brine A (see Figure 8 in Dresel and Rose.

<u>**Important Note**</u>: Your analysis is driven by the hypothesis that "connectivity between shallow and deep-subsurface waters in NE-PA" *allows groundwater contamination by gas company activity on a time scale that matters to mankind* (my words although this is implicit in your hypothesis). For your hypothesis that gas production activities are risky, it makes sense that free water circulation must occur in a very short

period of time relative to the geological time scale. So, the factor that makes your paper original is time, short time.   My analysis of your paper assumes that significant circulation can occur during post-glacial time which means less than, say, 10,000 years (call this modern time).   Otherwise, everyone agrees that there is connectivity over the long time frame and your paper would have nothing new to contribute.

<u>Third, there is the question of brine chemistry relative to mechanism of origin</u>. There is a difference in the chemistry of brines originating from the evaporation of sea water (the Dresel-Rose mechanism) and dissolution of the salts (the Harrison-Marshak mechanism).   The samples used in the Dresel-Rose analysis came from the western half of PA (more than 200 km from your sample localities). You cite Rowan et al (2011) as the source of your brine data and yet these samples for the most part come from the same area sampled by Dresel-Rose and could not have been effected by the Harrison-Marshak mechanism. The Rowan paper has at least 12 samples from NE PA area as well as several samples of the Hayes study. Do these show a different chemistry from those of western PA?   << One piece of geological terminology that is out of whack…. The formation is called the Lock Haven. Your use of the term Lockhaven is a time unit. >>

<u>**Important result from your data set**</u>: The distinction between the Dresel-Rose mechanism and the Harrison-Marshak mechanism is based on the fractionation of Br.   I am looking at Figure 8 from Dresel-Rose. Cl-Br follow mixing lines with the same slope during evaporation and dilution. However, when halite saturation is reached it can be seen that the crystallization of halite favors the fractionation of Br into the residual brine. This means that halite crystals are Br poor. The Harrison-Marshak model for dissolution of 7+ km^2 of salt which presumably includes a large fraction of halite would result in the formation of a brine depleted in Br.   That Br-depleted brine would have washed to the NW from the Lackawanna syncline and right through your sample area during the late Paleozoic Alleghanian Orogeny. You dismiss your Type C brines by attributing them to anthropomorphic activity and move on. I posit that washing 7+ km^2 of salt brine through Bradford County and vicinity during the late Paleozoic would likely result in some residual signal and you have found it.

<u>Fourth, there is the question of where <today> large volumes of natural, deep-basin brine might found that would cause salinization of groundwater by gas operations in the Marcellus</u>.   I think we could agree that the largest volumes of deep-basin brines might exist in the most porous of rocks in a basin. In the case of the Appalachian Basin, these sources might include such sandstones as the Oriskany, Medina, and within the karst of the Trenton-Black River carbonates. You will immediately note the correlation between these large-volume sources brine and gas-bearing formations. However, it is a mistake to assume that all gas-bearing source rocks host large volumes of natural, deep-basin brine. In fact, despite the significant porosity in gas shales, this porosity is largely oil-wet and nanometer scale pores within organic material. This porosity has virtually NO free water. In fact, high quality electric logs from the Marcellus show gas saturation greater than 95%. The 5% or less water saturation is all bound water. In principle, this is read as 5% of the 15% porosity in the Marcellus so that bound water constitutes 0.75% of the Marcellus by volume at most. Based on the free-circulation criterion established above, I hope that

we can agree that, in fact, there is NO such thing as large volumes of Marcellus brine as you have implied. Even the fractures in the Marcellus are charged with gas and not brine.

Important point: If there is no such thing as Marcellus brine, how can we presume that other brines can be compared with Marcellus brine or be 'Marcellus-like'? I don't know what water has been measured in your Figure 2 but it is clearly not modern-free-circulation Marcellus brine. Flowback water does not qualify as natural, deep-basin brine and I fear that you have mistaken flowback from the Marcellus as natural, deep-basin brine. The same is true for produced water from the Marcellus which most likely also originates partly as frack fluid. Again, electric logs show little free water in the Marcellus. Marcellus flowback and Marcellus production water is off the table in this discussion because this is not the natural pore waters that you are trying to document. Any natural water that is produced might have come from other formations like the Onondaga or Oriskany which is known to contain brine. This is why I suggested that you have crossed the line to the advocacy-based science with your term, 'Marcellus-like brine'.

<u>Fifth, there is a question of what might and what might not constitute a natural, deep-basin brine from a hydrological point of view</u>. I think we can agree that deep-basin brine is free water which is able to circulate, no matter the time scale. Under question #2 we have restricted circulation to modern times (< 10,000 years). Based on the modern-free-circulation criterion, I think we can agree that both bound water and water tied up in the crystalline lattices of clay do not constitute natural, deep-basin brines. Clay dehydration (e.g., smectite to illite) can give off enough water that evolves into a deep-basin brine but this is not on a time scale that matters. Such evolution implies dissolution of salt, but the Br/Cl does not allow much of this. The question of evolution of natural brine may seem like a trivial point but it has great bearing on question #4. This leads to the significance of both flowback and production water.

Important Point: It is true that brine is emerging when Marcellus is fracked. It is clear that early flowback water from the impermeable Marcellus shale is not true, natural deep-basin brine (yes, there may be occasional leakage from the Onondaga-Oriskany system but we don't have any way of knowing when). The best samples of nature, deep-basin brine come from production waters of the porous sandstones and fractured carbonates of the Appalachian Basin. The Dresel-Rose analysis relies exclusively on these latter samples to define the behavior of deep-basin brine. The way you have set the test for your hypothesis (i.e., sampling free-circulation groundwater), excludes the anthropomorphic brine from flowback and production waters from the Marcellus (and for that matter, the Utica). There is a distinction (or at least should be a distinction) between natural brine in the Appalachian Basin undisturbed by fracking) and the brine emerging from fracking and flowback of Marcellus

<u>Sixth, there is the question of whether electric logs are incapable of detecting free water in the Marcellus</u>. The answer is a resounding yes. We know that free water is found inside fluid inclusions within mineralized veins of the Marcellus. Interestingly, there is a pronounced change in the salinity of brine inclusions across the foldthrust belt, from 10-13 wt. % site BR, to 15-23 wt. % at site RA and to 24-26 wt. % at site EB, which is similar to brine inclusions in the Plateau. The highest salinity brines are interpreted

as basinal brines, while the lower salinity brines toward the hinterland may be related to mixing with either meteoric or migrating metamorphic fluids from the core of the orogen (Evans and Battles, 1999). You will note that Mark Evans is the expert on Marcellus fluids (via fluid inclusion work) and his work shows that fluids clearly passed through the Marcellus, but mostly during Appalachian tectonics more than 250 million years ago. Mark's work points to barium-rich fluids trapped during peak oil generation and migration but these were early fluids. There is no question that fluids were given off from the Marcellus at that time. However, fluid inclusions do not constitute free-circulation brines in the sense of your paper. Even if we do use fluid inclusions as the basis for defining a 'Marcellus-like' brine, Evans has shown that there is such a rich variety of fluids either originating from within or passing through the Marcellus that to define one of these fluids as "Marcellus-like" brine might be construed as cherry picking with an agenda outside of science.

<u>Seventh, there is the question of 'direction' of migration pathways</u>. The implications concerning brine migration in Dresel & Rose are clear. In short, brine, which originated as evaporated seawater in the Salina salts, migrated upward in the Paleozoic section from the Salina Salt. This implies that the entry composition of brine before upward migration is their type A brine (Dresel-Rose Figure 8). The most vigorous upward migration was periods of tectonic activity characterized by Oliver's (1986; Geology) model for fluids expelled from orogenic belts (this may or may not be a consequence of hydrodynamic flow). The period of activity characterized by Oliver's model was the period when fluids passed through the Marcellus as discussed in question #6. Even then there must have been dilution from downward circulating groundwater. So, once the Alleghanian orogeny came to an end, the brine salinity was set in the Paleozoic section up through Carboniferous rocks. With the cessation of Alleghanian tectonics, dilution started in earnest and this is the mixing curve shown in Dresel-Rose (Figure 8). Dilution was largely a consequence of the downward migration of freshwater into the brines of the Salina salt after they were scattered throughout the Devonian section above. This distinction is subtle but important because you imply dilution by brine moving into a stationary fresh water (your page 9). Rather, hydrodynamic flow moves freshwater into rocks with more saline brine. It seems to me that freshwater infiltration into elevated areas will mix with brine as it advances, but also will push the brine toward outlet areas in river valleys, and cause mixing with fresh water in that area. Your samples demonstrate this phenomenon and this has nothing to do with 'vertical' migration from some deeper source.

<u>Eighth, there is the question of the drive mechanism for delivering deep-basin brines to groundwater on modern (< 10,000 year) time scales</u>. 1.) I think we can agree that the energy source for hydrodynamic flow is gravity. Toth (1962) makes it very clear that gravity-driven flow path that is as deep as the Marcellus requires millions of years and is thus not modern. There are well known salt seeps on the Allegheny River, and evidence for brine seepage in valleys elsewhere in the region, such as Bald Eagle Valley. So, there is good evidence for current gradual movement of brine but driven by elevation head which dictates a relatively shallow flow path over a time interval that matters. Even then, the subtle topography of the Appalachian Mountains might preclude seeps from the Marcellus emerging much short of the coastline. 2.) If gravity-driven energy is off the table, then glacial rebound might be a candidate but you have cited papers that show circulation limited to about the top 500 meters in modern times and thus incapable of driving brine from the Oriskany, for example. 3.) I should point out that you misuse the

term hydrodynamic pressure as defined in early papers by Hubbert and Toth. What you mean is that the Marcellus gas is overpressured as a consequence of thermal maturation. In fact, this overpressuring is responsible for generation of natural hydraulic fractures and subsequent leakage of vast quantities of petroleum and natural gas. However, the overpressure of gas in the Marcellus is irrelevant if there is no natural brine to drive from the Marcellus (my point in question #5). Brine might be driven from the Oriskany but it has to pass through the hundred plus meters of Marcellus which continues to act as a seal to keep a significant quantity of Oriskany natural gas in place (or at least did so until the Oriskany gas was produced).

<u>Nineth, there is the question of the mechanism for fluid stability in the crust that preempts delivery of deep-basin brine on a modern time scale (i.e., buoyancy)</u>. Everyone agrees that buoyancy is responsible for gas moving through a matrix that literally acts as a filter to brine migration. Hence, the operators have encountered gas in every sand layer with slightest porosity. You are aware that DEP has released data showing free gas in more than 50 sand layers between the Marcellus and the surface. However, buoyancy acts to keep deep-basin brine in place. You are also aware that groundwater forms stable layers in the upper crust based on density distribution and that density increases with salinity. This is why it is extraordinarily rare to sample brines in the top 500 feet of NE PA (as your data show). I would even go so far argue that your Figure 2 demonstrates why your hypothesis for industry driven brine contamination is unlikely. It is very difficult if not impossible to upset the density stratification of groundwater to deep-basin brine, particularly when you consider the scale of the potential industry impact compared with the scale of the basin. There is not enough of a delta energy to do it. The there is also a mass balance problem. If you seek a model that drives brine upward on short order you must add something where the brine was. Even if something is added it might act to lift overburden rather than displace brine. The point is that your data demonstrate that shallow hydrodymanic flow (salt in the valleys) and not buoyancy is responsible to Appalachian Basin circulation.

<u>Tenth, there is the question of the transient pressure drive during well stimulation</u>. We all agree that the Darcy flow laws for groundwater govern the process by which fluid might migrate. Matrix permeability is insufficient to permit Darcy-flow on time scales that matter. Consequently, we have to look at fractures as the only path with enough permeability to matter. Even here, pressure during well stimulation does not drive (or open) fractures beyond about a 1000 foot halo. Surface pumps cannot deliver enough energy to drive fractures beyond a thousand vertical feet even if industry wanted to do it. Once the stimulation ends, the pressure gradient is back into the well bore, thus ending any possibility for any pressure of modern-free-circulation brine drive along natural fractures.

<u>Eleventh, there is the question of ages of deep-basin brines</u>. We have all agreed that deep-basin brines don't move much. In every sedimentary basin I am aware of, when folks age-date the deep brines (at Marcellus depths), they get literally formation age water. Millions of years except at the basin edges where occasionally glacial meltwater has diluted the brine. This was found by the USGS in the Illinois Basin and by the Michigan group in the Michigan Basin. Siegel (Syracuse) found melt water in Lockport

dolomite, diluting the Appalachian Basin type brines found in this rock at several hundred feet depth. But these brines do not MOVE in the formation. The dilute water much farther up does. Rather, the brines do move, but at extremely slow, geologically slow, flow rates. Modeling has shown this in spades in basins everywhere as indicated above.

Twelveth, there is question about the need to mention abandoned wells (your page 9). Abandoned wells and an elevated brackish water table should not correlate. If anything production promotes inward flow which should depress the brackish water tables. You were sampling in an area of PA where there are very few abandoned wells, so it seems unlikely that your water chemistry is being affected by the short circuit that abandoned wells might present between deep brine and fresh water. We all agree that there is a risk from abandoned wells but your sampling program presumes that there are natural pathways, so even mentioning abandoned wells is a red herring that muddies the waters. It is true that there are a number of documented localities where highly saline Ba-rich water is emerging from abandoned gas wells. This does mean that the deep brine is at heads greater than shallow groundwater but because of elevation effects on the deep brine aquifer. While these head differences are sufficient to drive brine in an abandoned well, matrix permeability without the benefit of abandoned well preempts meaningful flow on a time scale that matters.

Important note and in summary. I have posed a dozen questions that must be answered. Does your data address any of the twelve? Without answers to the questions that I have posed your paper does not make a meaningful test of your hypothesis that "connectivity between shallow and deep-subsurface waters in NE-PA" *allows salinization of groundwater by gas company activity on a time scale that matters to mankind*." To close on a positive note, you have a very exciting result in a verification of the Harrison-Marshak model, and I wish that had been the subject of your paper. You would then have then made a significant contribution to understanding of the Appalachian Mountains.

There are issues concerning the geochemistry of the Appalachian Basin that require further thought:

Barium and other trace metals also are found through-out the Paleozoic stratigraphic section of the Appalachian Basin. The Marcellus has barite nodules in it and in fracture cementation over geologic time. So much barium occurs naturally in Devonian shales in general that the occurrence of Ba and other trace metals associated with the shales can be tracked in the ostoliths of fish which happen to hang out along the Mohawk where the shales crop out (Limburg papers). So Ba in waters cannot be tied to the Marcellus as a clear "fingerprint". It can come from other formation. Strontium too. Celestite even occurs in the section.

The water isotopes of the Appalachian Basin brines, in contrast, vary quite a bit, depending on the extent to which evaporation of seawater originally sequestered heavier isotopes in precipitations in the evaporative basin (This is where the Silurian Salina salt really dominates the geochemistry of the entire basin). Water isotopes show great variability, even within permeable brine filled gas formations like the Medina. To expect clear signals in water isotopes vertically in the sedimentary pack would be most unusual--other than obvious glacial meltwater impact.

Terry Engelder, Penn State